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ONR CONTRACT

N00014-87-J-1275

PULSED PLASMA PREPARATION
FOR LWIR MATERIALS

FINAL REPORT

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STC TECHNOLOGY LTD

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The objective of this programme was to apply the capabilities of the novel STL pulsed plasma process to the preparation and screening of new infra-red materials. The area of specific interest is transmission window materials for the far infra-red (8-12 micron), which perform better than ZnS in at least one respect, without any trade-off in other properties.
Eight binary phosphides, novel in both composition and structure, have been investigated for use in IR applications. Excluding cadmium phosphide, in which the band gap was too small, all the phosphides are harder than ZnS. In addition, most are IR transparent in the regions of interest, though hydrogen inclusion tends to occur in those phosphides with the lighter cations (causing absorption near 12 micron) and silicon and aluminium phosphides exhibit absorption. Aluminium phosphides have for the first time been made stable, at least at the higher phosphorus contents, and addition of zinc to silicon phosphide has demonstrated the potential of ternary additions in beneficially modifying absorption characteristics and mechanical properties. In view of the latter data, the ternary zinc germanium phosphide offers great potential. This ternary is expected to be harder than either binary, with a larger band gap, and any weak absorptions beyond 12 micron are expected to move further away. Gallium phosphides are also still of interest, but are considered of lower priority.

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NWC Contract N00014-87-J-1275
PULSED PLASMA PREPARATION FOR LW-IR MATERIALS

SUMMARY

The objective of this programme was to apply the capabilities
of the novel STL pulsed plasma process to the preparation and screening of
new infra-red materials. The area of specific interest is transmission
window materials for the far infra-red (8-12 μm), which perform better than
ZnS in at least one respect, without any trade-off in other properties.

The work reported here has targeted a new class of amorphous
super-phosphides as having significant potential as IR materials, and has
developed these materials in three stages.

1)   Proof of concept on a model system
2)   Screening of the potentially useful members of this class
3)   Evaluation of ternary compounds, and selection of an overall
      winner

Due to a reduction in funding in the last year of the
programme, stage 3 did not select an individual winner, but the
super-phosphides of Ge, Ga and Zn have been selected as worth further
investigation.

Prepared by   : G. A. Scarsbrook
Approved by   : R. A. Heinecke
Authorised by: P. W. Graves
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CONTENTS

LIST OF TABLES AND FIGURE CAPTIONS

Table 1:   Table of the binary and ternary phosphides examined during
1988-89, showing and measured band gap (i.e. energy at $\alpha=10^3$
and $\alpha=10^4$, see text) and Vickers microhardness data (50g load,
10 seconds application).

Figure 1:   A plot of the variation in band gap, measured by the 5%
transmission point, of germanium phosphide as a function of
composition. Also included are two data points from the
ternary GePS, showing the enhanced effect of S over P in
increasing the band gap.

Figure 2:   Infra-red transmission curves of $GeP_{3.5}$ showing the film i) as
deposited, ii) after annealing at 300°C for 1 hour, and
iii) after water immersion for 1 hour. The latter two curves
are displaced along the Y axis by 20% and 40% respectively for
clarity.

Figure 3:   Infra-red transmission curve of a 20μm film of GeP_2S on a Ge
substrate.

Figure 4:   Plot of the measured bandgap data (i.e. energy at $\alpha=10^3$ and
$\alpha=10^4$, see text) of the binary and ternary phosphides, before
and after annealing in N_2 at 300°C for 2 hours.

Figure 5:   Infra-red transmission curve of 3.8 μm CP_{13} film on Ge, with Ge
substrate background curve subtracted.

Figure 6:   Infra-red transmission curves of 4 μm AlP_{13} film on Ge, with Ge
substrate background curve subtracted. The upper trace shows
the film as deposited, whilst the lower trace shows the film
after a 2 hour water immersion.

Figure 7:   Infra-red transmission curve of a 2.9 μm $ZnP_{3.5}$ film after an
anneal at 400°C for 2 hours.

PULSED PLASMA PREPARATION FOR LW-IR MATERIALS

1.   OBJECTIVE

The objective of this programme has been to prepare and
evaluate new long wavelength infra-red transparent materials, using the
novel high energy pulsed plasma technique developed at STC Technology Ltd
(STL) . New materials are required to out-perform the current materials
(ZnS) in at least one aspect, without any trade-off in the other
properties.

2.   INTRODUCTION

The 8-12 μm window material predominantly used in current IR
applications is ZnS, since this material exhibits the best available
compromise between the properties required. However, the rain erosion and
thermal shock performance of ZnS is insufficient to satisfy the
specifications of all current and future applications, and it starts to cut
off in transmission before 12 μm at operating temperatures above 700°C.

Many years of research using conventional preparation
techniques have failed to identify a replacement material for ZnS, in part
due to the time required in conventional processing techniques, and partly
because of their limitation to thermodynamically stable phases. A possible
exception to this generalisation is CVD diamond film, and hence there has
been rapid growth in this area although practical diamond domes are still
very distant.

The novel pulsed plasma deposition process, developed at STL,
is an ideal tool for rapid preparation and evaluation of new materials.
This programme has used pulsed plasma for the rapid development of new
infra-red transparent materials. The search is targeted particularly on
bulk materials for the 8-12 μm window to replace ZnS. Details of the
pulsed plasma technique are given in Appendix A.

A new class of amorphous phosphorus-rich phosphides has been
identified, with considerable promise for a replacement for ZnS. Members
of this class of materials which are of particular interest are ZnP, GeP,
GaP, and the ternaries ZnSiP and GePS.

3. PHOSPHORUS RICH PHOSPHIDES

3.1 Design of New LW-IR Materials

The study for new IR materials has to find a compromise to the
two conflicting needs:

i) IR transmitting materials must have weak covalently bonded
structures, low atomic co-ordination, and heavy atoms, in order to
avoid phonon absorption within the IR window required.

ii) Conversely, for both strength and for a wide band gap to avoid free
electron absorption as the temperature rises, the material requires
strong bonds and light atoms.

For window applications, the mechanical properties of the
window material are as important as the IR transmission. The use of a
heavy anion results in poor mechanical properties and a low band gap
because of the d electrons. This would suggest that phosphorus and sulphur
are the only choices for the anion, relying on a heavy cation to lower the
phonon frequencies. It is, perhaps, not surprising that zinc sulphide has
to date been so successful as a window material.

Phosphorus is a unique element, capable of forming similar
fully bonded structures in both crystalline and X-ray amorphous forms.
This enables defect free binary materials to be produced in amorphous form
by PACVD techniques. The thermal stability of elemental phosphorus varies
enormously depending on the particular allotrope, but continuously bonded
three-dimensional networks, such as found in black phosphorus, are quite
stable. This type of bonding, in conjunction with the correct cation
addition, can result in amorphous structures which are hard, have a
moderately wide band gap, and transmit beyond 12 μm. A literature study of

phosphorus and its compounds is presented in Appendix B.

Sulphur does not have the same potential as phosphorus for forming single anion amorphous materials, since its two bonds make it chain forming rather than network forming. Mixed phosphide/sulphides have proven inferior to phosphides, during this programme (Sec. 3.2), due to IR absorption near 12 μm.

The experimental work on phosphides was split into three stages:

1) Evaluating the effects of composition and sulphur additions in the model system GeP_xS_y.

2) Screening the phosphorus-rich binary compounds.

3) Studying selected ternary compounds.

3.2 Stage 1: Deposition and Characterisation of the Model System GeP_xS_y

In the first stage, completed mainly in 1988, GeP and GePS were prepared in a wide range of compositions as homogeneous, amorphous, well-adherent films onto silicon or germanium substrates. The properties of the films were shown to vary continuously with composition, and in particular the band gap of GeP_x could be varied from ~ 0.9 to 1.6 eV, as x varied from 0.5 to 6 (Figure 1). GeP_x showed no specific absorption peaks between 3 and 20 μm, down to a resolution of < 5 cm^{-1}, with excellent chemical stability (Figure 2), and a hardness of ~300 Hv. Additions of sulphur were shown to increase the band gap ~5 times as quickly as P, but also to add weak IR absorption at 12 μm and beyond (Figure 3). Scratch testing identified that as S was added to GeP the hardness of the film decreased to a minimum and then started to recover again. Annealing of the films was shown to increase the band gap by ~ 0.15 to 0.3 eV, which was modelled as an increase in chemical (bonding) order [1].

3.3 Stage 2: Screening of Binary Phosphides

Stage two, commenced in 1989, was a rapid screening of the other binary materials; BP, CP, AlP, SiP, ZnP, GaP, and CdP although the latter was later excluded because of its low bandgap. Of these, both AlP and SiP have shown intrinsic absorption in the 8-12 μm window; these compounds also showing some long term instability.

In preparation for the deposition of the phosphorus-rich binaries, the deposition of phosphorus was first investigated. It was found that the deposition rate was critically affected by the dc bias generated on the RF electrode, even when using the hollow electrode configuration. The phosphorus was apparently re-sputtered when the bias was high, or when a buffer gas of Ar was used; and an He buffer gas was required. Consequently, exclusion of hydrogen was difficult in pure phosphorus films (though the majority annealed out), but the optical band gap was found to be encouragingly large (1.72 eV at α=10^4) with a well defined cut-off, and IR transmission data showed transmission to beyond 20 μm, with no evidence of intrinsic absorption. These results are in agreement with reported IR absorptions [2], namely:

P-P	510-390	cm^{-1}	measured
	450	cm^{-1}	calculated
P-H	2457-2240	cm^{-1}	stretch } measured
	1150-800	cm^{-1}	deform }

When depositing the binary phosphides in the hollow electrode, the apparent sputtering of phosphorus was not observed, presumably due to the greater stability of the binaries, and deposition conditions could be better optimised. However, not all of the binaries were produced entirely hydrogen-free. Some of this problem early in the year was due to failure in the RF generator, resulting in lower power levels than indicated, and leading to incomplete dissociation. However, even at higher power levels a small amount of hydrogen remained in the BP and SiP, though particularly in the SiP this could be largely annealed out. Hydrogen in these materials results in two absorption peaks, near 4.5 μm and 11-12 μm, the latter peak being confirmed as hydrogen by the correlation between its intensity and

that of the former peak during annealing. Hydrogen retention in BP is
perhaps not too surprising, since the B-H-B bridge is very stable, but the
reason for hydrogen inclusion in SiP is uncertain.

Table 1 shows all the binary phosphides deposited, giving band
gap and hardness data. Figure 4 displays graphically the band gap data for
direct comparison. The band gap data in this work has been obtained by
observing the energy at which the optical absorption coefficient α reaches
10^3 and 10^4, these being typical values of α at the band edge as predicted
by the various theoretical models [3]. This approach is used in preference
to complex analysis such as a Tauc plot which, based on a particular model,
may be in error and therefore misleading. Recording the energy at two
absorption values allows the sharpness of the band edge to be measured.
Details of the phosphides prepared are given below:

3.3.1 Boron Phosphide

Reported IR data: [2]

P-B	750-550	cm^{-1}	measured
P-B	1500-1400	cm^{-1}	measured
P-B	666	cm^{-1}	calculated

Experimental Data: Boron phosphide is a difficult material to
prepare in bulk for IR applications by methods other than CVD. Its
application may be limited by weak absorption near 12 μm, though this
probably results from hydrogen inclusion. As noted earlier, all BP films
prepared in this programme have shown significant hydrogen absorption in
this region, but effort was concentrated on other phosphides since BP was
being evaluated elsewhere.

3.3.2 Carbon Phosphide

Reported IR Data: [2]

P-C	780-620	cm^{-1}	measured
	719	cm^{-1}	calculated
P-CH$_2$-P	845-795, 770-720	cm^{-1}	measured
P-C	1230-1180	cm^{-1}	measured

Experimental Data: The observed deposition rate of carbon phosphide was found to be anomalously low, and the measured composition of the film deposited was not that expected. In particular, even at gas compositions corresponding to near CP_1, the film composition was $CP_{>12}$. This effect appeared initially to result from mutual etching of carbon and phosphorus, though later results are more ambiguous and have made evaluation of this binary difficult.

Despite these difficulties, no intrinsic absorption has been observed in CP films; the absorption at 750 cm^{-1} (Figure 5) is probably hydrogen, resulting from the constraints on the deposition window. Annealing of CP films, shifts the optical cutoff a long way into the blue, suggesting that major structural changes occur, and perhaps suggesting that full bonding does not occur during deposition.

Carbon can also be incorporated, to at least 10% levels, in ternaries from organo-metallics (e.g. containing Al and Zn), where no IR absorption or other detrimental effects associated with the carbon are seen. Some mutual etching of phosphorus and carbon occurs in these cases, resulting in a film stoichiometry different to the gas composition, but in a manner which is repeatable and largely predictable.

3.3.3 Aluminium Phosphide

Reported IR Data: [2]
Al-P 406 cm^{-1} calculated

Other Reported Data: AlP is normally considered chemically unstable with respect to hydrolysis and formation of PH_3 as a result of the exceptional stability of Al_2O_3 (and consequently it is often used as a fumigant). Its stability is thought to increase with purity. The thermal conductivity of crystalline AlP is high (~1.3 $Wcm^{-1}K^{-1}$ at room temperature).

Experimental Data: Initial films of aluminium phosphide, deposited from trimethylaluminium (TMA) and PH_3, were unstable at all compositions, as were ternaries such as AlGeP. By using a capping layer of

GeP on an AlP film, an IR transmission curve of AlP was obtained. This curve showed only weak absorptions in the 8-12 μm window, which were thought to be extrinsic, and this encouraged further development. Following the repair and recalibration of the RF generator, so that higher power levels were achieved, AlP_x films with x>7 were deposited which were stable in room air (~1 week), water (~2 hours, see Figure 6), and nitrogen gas annealing up to 300°C (small unidentified peaks arising at 400°C). However, at compositions below ~AlP_4 the films were still unstable, hydrolysing in room air, and the long term stability of higher aluminium phosphides is in doubt. IR spectroscopy shows an apparently intrinsic absorption starting weakly near 800 cm^{-1} and strengthening towards 400 cm^{-1}. At lower deposition rates, carbon inclusion can be kept very low (<1%). However, at higher deposition rates (>0.5 Å per pulse) significant carbon is incorporated, though this appears not to affect the stability. The hardness of an – AlP_7 ($C_{<0.3}$) film was measured as 388 Hv, though the film showed significant brittle cracking at the indentation corners. Higher hardness values may be obtainable with compositions nearer AlP, but have not been measured because of the instability of the material.

3.3.4 Silicon Phosphide

Reported IR Data: [2]

P-Si 515-414 cm^{-1} measured
      434   cm^{-1} calculated

Experimental Data: The experimental data for SiP is described with the ternary materials in Sec. 3.4.

3.3.5 Zinc Phosphide

Experimental Data: ZnP_x compounds are particularly easy to deposit, free of hydrogen and with the IR transmission curve showing only a small sharp peak at 900 cm^{-1}. This peak is thought to be extrinsic, but currently is unidentified. At low deposition rates carbon can largely be excluded from the films, but at moderate rates (0.5 Å/pulse) carbon is incorporated, but does not appear deleterious to the film. This is similar behaviour to that seen with the AlP_x growth. Films of ZnP are stable in

water and after annealing at 300°C (Figure 7). Hardness testing measured
276 Hv but showed significant brittle or interface failure; the latter
would result in a low value. For comparison, optical quality ZnS was
measured as 190 Hv by the same technique.

3.3.6 Gallium Phosphide

Reported IR Data: [2]

P-Ga 370-320 cm^{-1} measured
  339 cm^{-1} calculated
Bulk GaP absorbs at 366 cm^{-1}

Other Data: Gallium phosphide is well known as a bulk
crystalline semiconductor. Its thermal conductivity is then 1.0 $Wcm^{-1}K^{-1}$,
the band gap 2.25 eV, the hardness 845 Hv and the refractive index 2.9.
Bulk GaP is being evaluated under the ONR programme as an IR dome material,
where its main limitation would appear to be absorption at the long
wavelength side, particularly as the temperature increases above 500°C.
This problem may be reduced in amorphous material.

Experimental Data: Amorphous phosphorus-rich GaP is similar to
AlP and ZnP in deposition conditions and behaviour with deposition
parameters. The IR transmission spectrum shows absorption starting above
10 μm due largely to hydrogen (Figure 8), which can be partially annealed
out at 400°C, and largely removed at 500°C. Higher RF pulse powers may
cure the hydrogen inclusion. The environmental tests (water, moist room
air) do not result in any change in the IR spectrum, but the material does
emit an odour of phosphine, so long term stability needs further
evaluation.

3.3.7 Cadmium Phosphide

Initial work on cadmium phosphide showed that the band gap was
very small, resulting from the heavy cation, and this material was excluded
from further analysis.

3.4   Stage 3: Evaluation of Ternary Compounds

Stage three compared the ternary ZnSiP with the two component binary phosphides. Figure 9 shows a SiP_2 film as-deposited, as-annealed, and compared with a $ZnSiP_{3.5}$ film. The following points can be noted:

a)   Even at higher powers, up to 30 kW, some hydrogen was always incorporated in SiP, giving rise to peaks at ~2200 and ~700 cm^{-1} which largely annealed out at 400°C and above.

b)   Intrinsic absorptions in SiP are seen at ~500 cm^{-1} (fundamental: very strong) and 1000 cm^{-1} (harmonic: moderate). The latter peak, however, decreases slightly with annealing at 400°C, and further at 500°C to about half its initial intensity. In addition, in more phosphorus-rich compositions, the 1000 cm^{-1} peak is proportionately weaker than the 500 cm^{-1}.

c)   Addition of Zn to SiP moves the harmonic SiP absorption to longer wavelengths.

These observations make SiP a very interesting system to study. Since SiP shows good mechanical properties (e.g. 420 Hv), if the harmonic absorption peak can be moved entirely out of the IR window by ternary additions, then SiP based ternaries could be important. More probable, however, is that the SiP system could enable rapid study of this type of chemical addition effect, which in turn could be applied to other binaries such as $ZnGeP_{2x}$.

4.   CONCLUSIONS

Eight binary phosphides, novel in both composition and structure, have been investigated for use in IR applications. Excluding cadmium phosphide, in which the band gap was too small, all the phosphides are harder than ZnS. In addition, most are IR transparent in the regions of interest, though hydrogen inclusion tends to occur in those phosphides with the lighter cations (causing absorption near 12 μm) and silicon and aluminium phosphides exhibit absorption. Aluminium phosphides have for the

first time been made stable, at least at the higher phosphorus contents, and addition of zinc to silicon phosphide has demonstrated the potential of ternary additions in beneficially modifying absorption characteristics and mechanical properties. In view of the latter data, the ternary zinc germanium phosphide offers great potential. This ternary is expected to be harder than either binary, with a larger band gap, and any weak absorptions beyond 12 μm are expected to move further away. Gallium phosphides are also still of interest, but are considered of lower priority.

REFERENCES

1.   G. Scarsbrook, I. P. Llewellyn, R. A. Heinecke, J. Vac. Sci. Technol. A 7(3), June 1989, p1099.

2.   D. E. Corbridge, Topics in Phosphorus Chemistry, Vol. 6, Series Editors, M. Grayson and E. J. Griffith, Interscience (1975).

3.   N. F. Mott and E. A. Davis, Electronic Processes in Non-Crystalline Materials, 2nd Edition, International Series of Monographs on Physics, Series Eds. W. Marshall and D. H. Wilkinson, Clarenden Press, Oxford, 1979.

Binary addition	Band gap (eV)		Hardness* Hv (50g)	Comments
	E at $\alpha=10^3$	E at $\alpha=10^4$		
B	$BP_{1.7}$ 1.33 (1.46)	1.72 (1.77)	$BP_{1.7}$ 806 (759)ⁱ	n = 3.1 ± 0.1 High power required to exclude hydrogen
C	CP_{13} 1.24 (1.72)	1.70 (2.30)	-	Mutual etching of C & P
Al	AlP_7 1.35	1.65	AlP_7 388	AlP_x, x ≥ 7, stable ≥ week
Si	SiP_{12} 1.46 (1.73)	1.89 (2.08)	SiP_2 420	Some adhesion problems. Indication of long term instability. n = 2.9 ± 0.1
P only	1.72	1.97	-	Difficult to deposit (sputtering). Some hydrogen inclusion.
Zn	$ZnP_{3.5}$ 1.61 (1.61)	1.91 (1.93)	~ZnP_2 276	
Ga	$GaP_{1.9}$ 1.49 (1.51)	1.80 (1.81)	$GaP_{1.9}$ 729	
Ge	GeP_3 - (1.03)	1.08 (1.35)	(~300)	
Cd	CdP_3 1.22	1.43		
ZnSi	$ZnSiP_4$ 1.46 (1.62)	1.80 (1.92)	559 (453)ⁱ	n = 3.0

*ZnS measured as 190 Hv   ( ) = anneal 300°C/2hr in nitrogen   ⁱSuspected adhesion failure

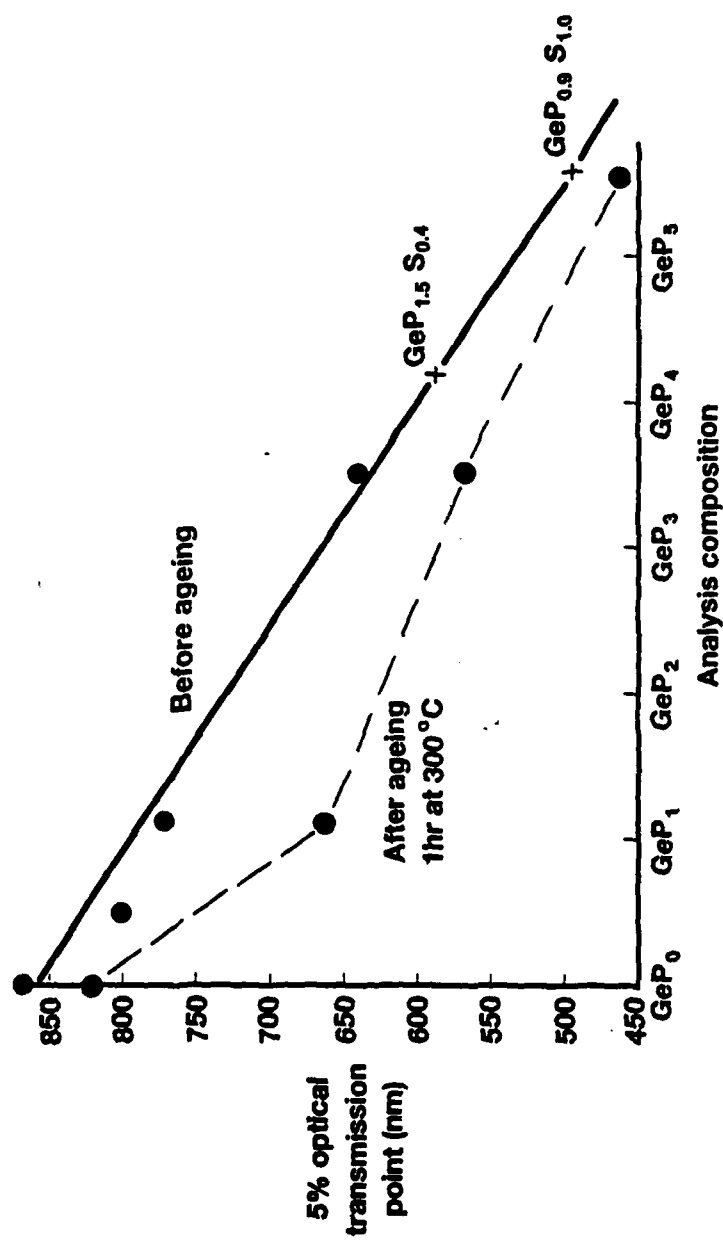Table 1: Band Gap and Hardness Data for the Binary Phosphorus-Rich Phosphides

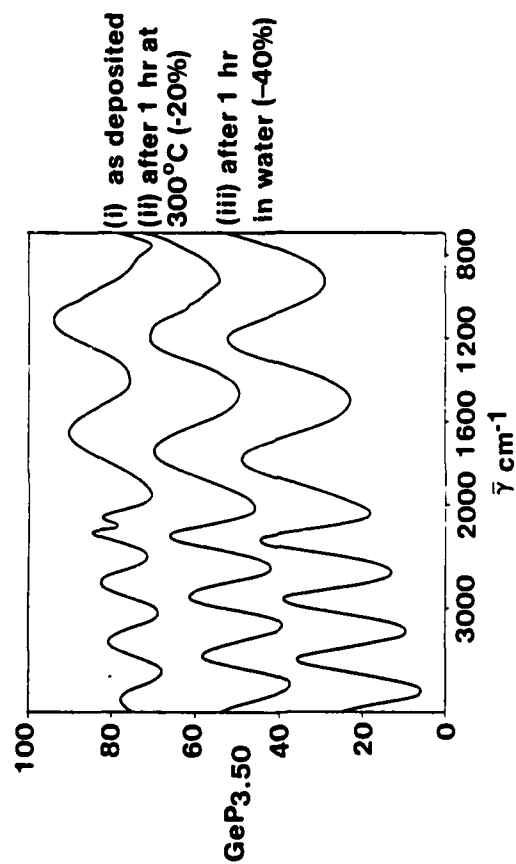Figure 1: Variation of 5% Optical Transmission Point with Composition in GeP$_x$

13

Figure 2: IR Transmission Spectra of GeP$_x$S$_y$ Thin Films after Various Treatments
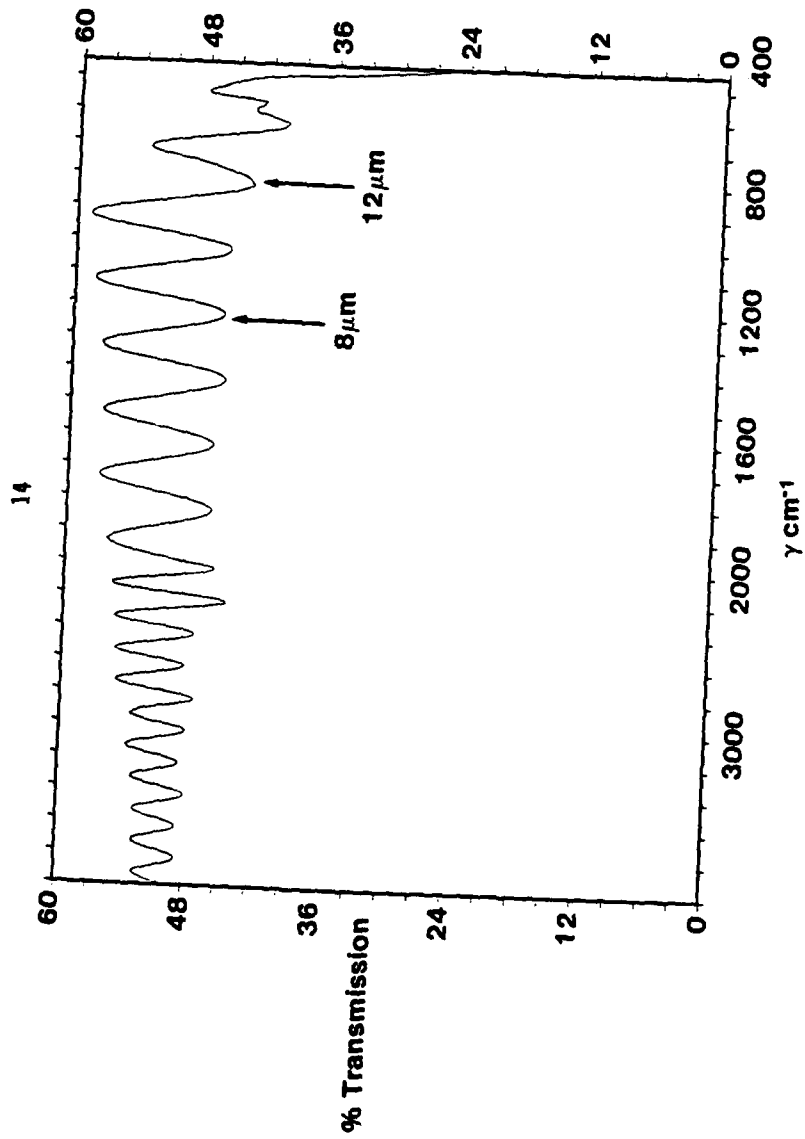
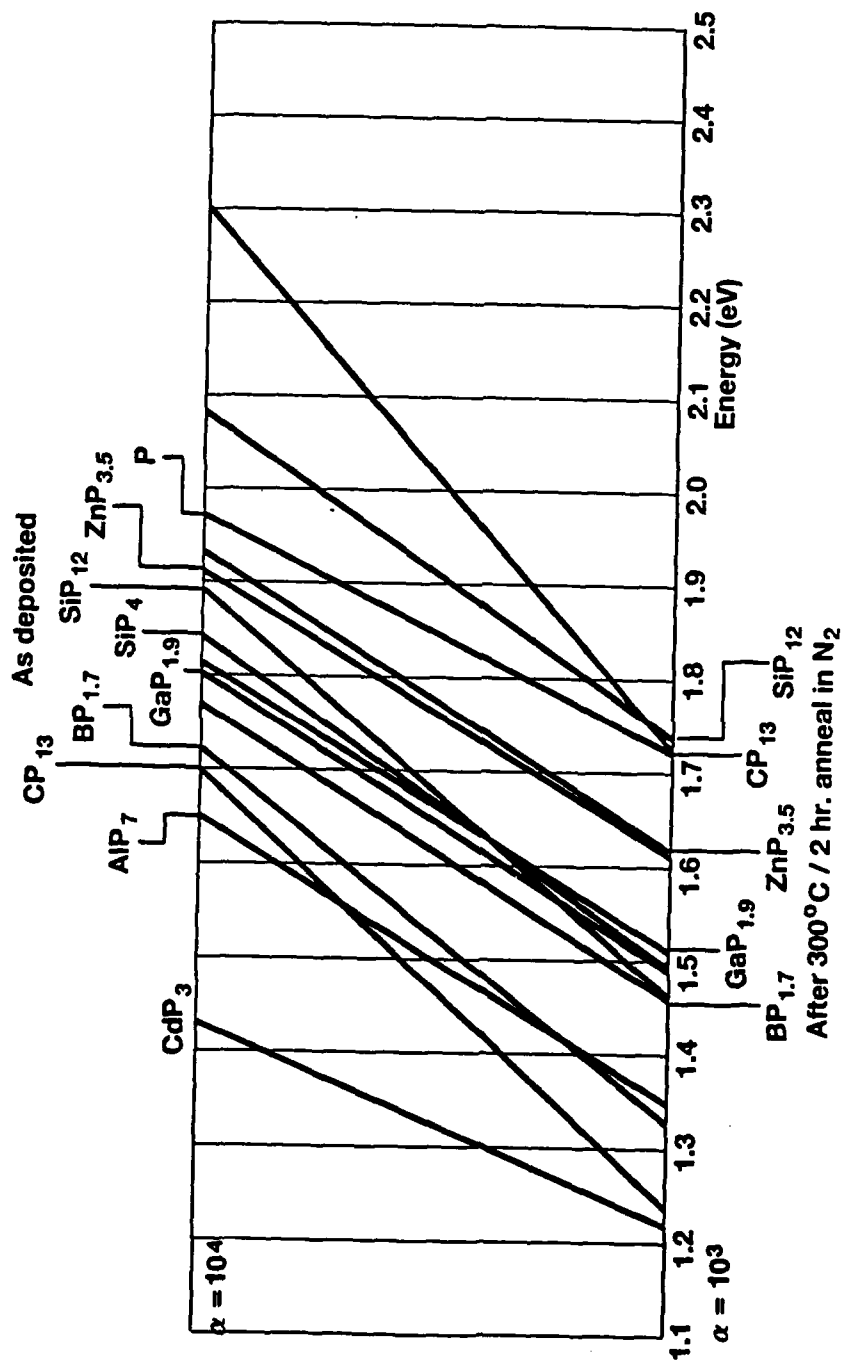Figure 3: IR Transmission Spectra for 10 μm Thick Film of GeP₂S

15

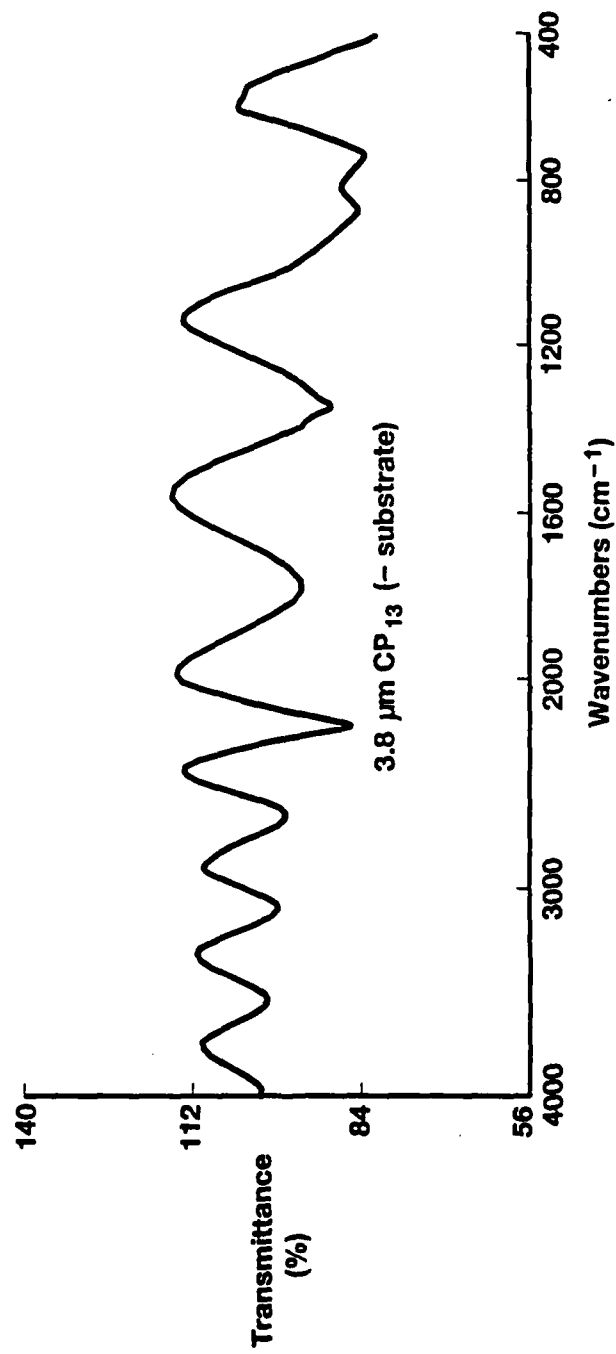Figure 4: Optical Absorption Edge Characteristics of Binary Super-Phosphides before and after Annealing

16

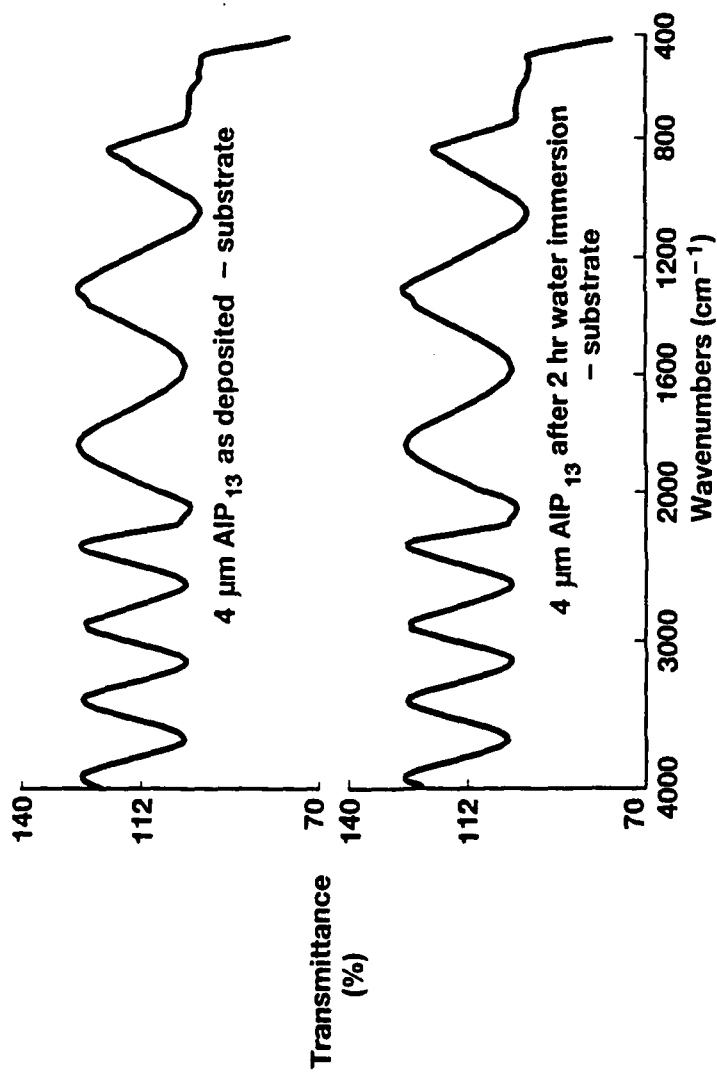Figure 5: IR Transmission Spectrum for 3.8 μm CP₁₃ on Ge

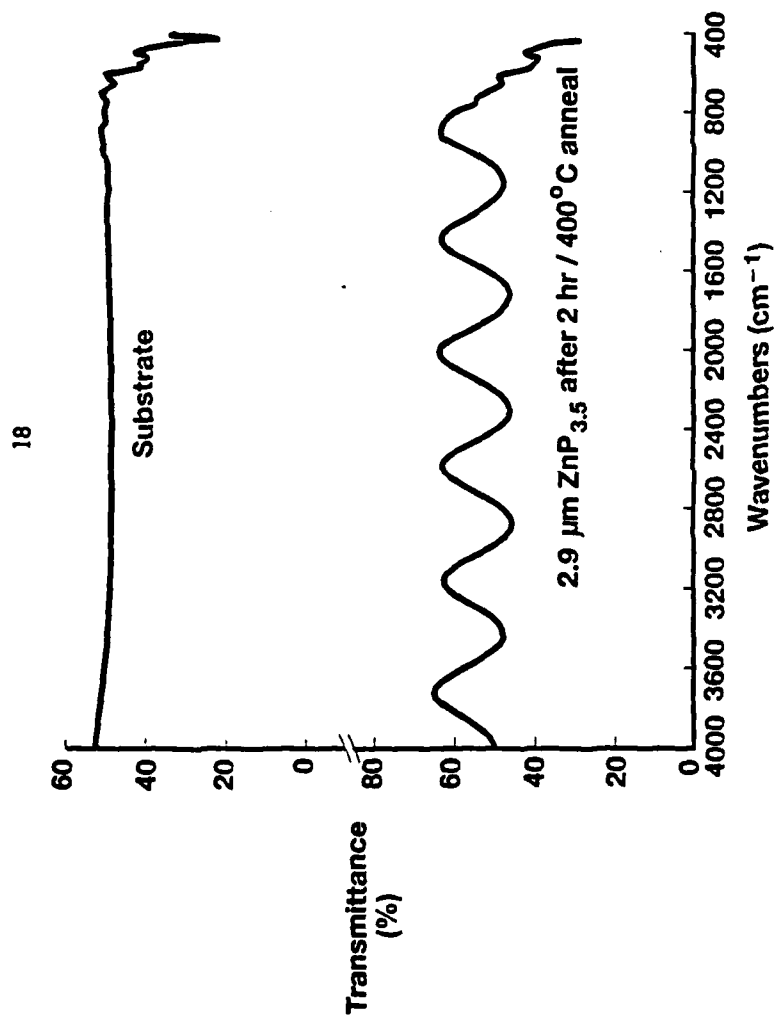Figure 6: IR Transmission Spectra of AlP Before and After Annealing
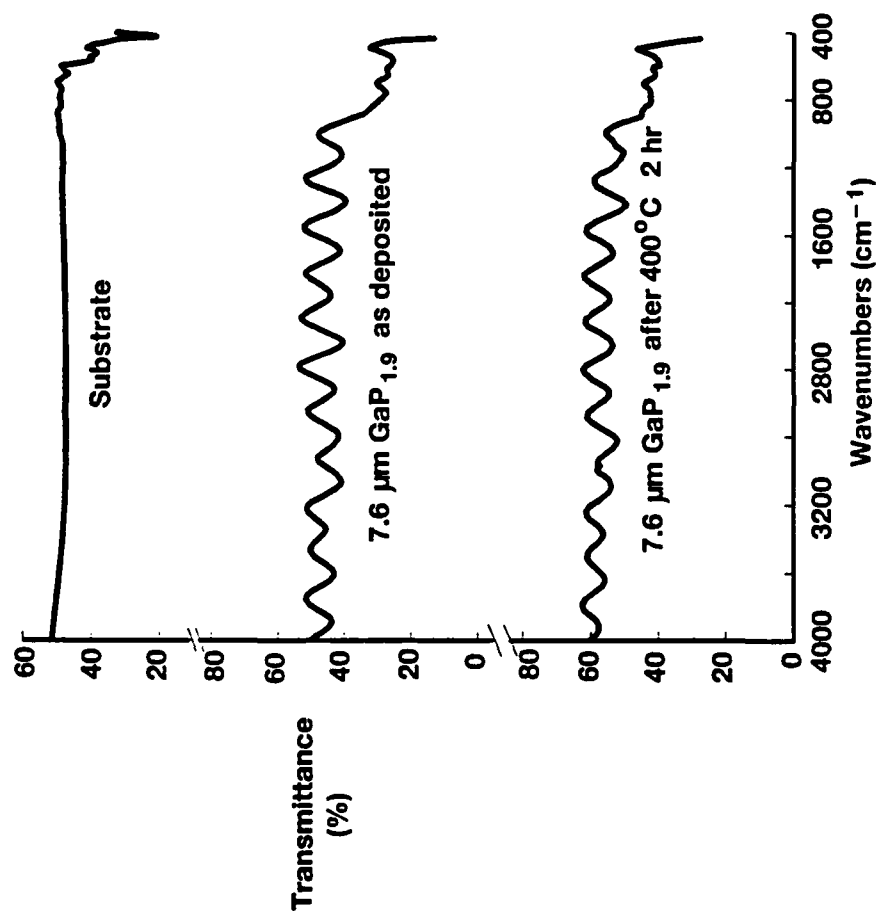
Figure 7: IR Transmission Spectra of ZnP After Annealing

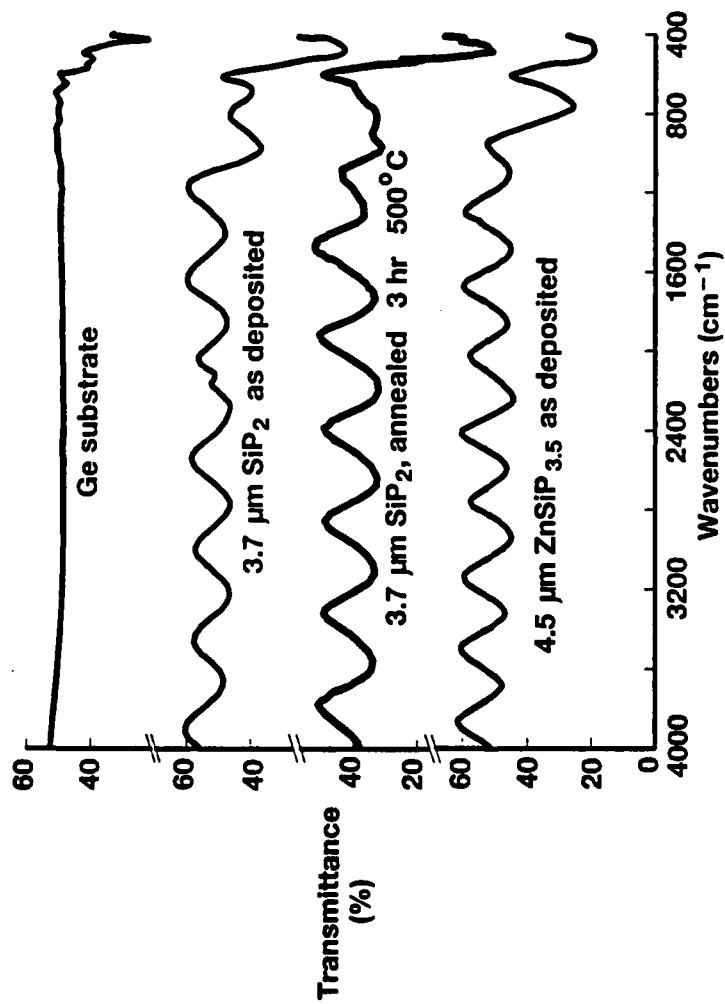Figure 8: IR Transmission of As-Deposited and Annealed GaP

Figure 9: IR Transmission Spectra of SiP and ZnSiP

APPENDIX A

DEVELOPMENT OF PULSED PLASMA EQUIPMENT AND PROCESS

A1 BASIC ARRANGEMENT

Pulsed plasma deposition uses high powered RF pulses to fully dissociate precursor gases at low pressure, causing atomic deposition onto a substrate.

The plasma reactor used is in the form of a 6-way 100 mm diameter cross, with electrodes entering from the top and bottom, gas flow from right to left, and a viewing window at the front (Figure A.1). Gas pumping is by a roots rotary combination with nominal pumping speed of 500 m^3h^{-1}. Typical operating pressures are 50-300 mTorr, as measured by a capacitive manometer connected directly to the chamber. The pumping speed at the chamber is controlled by an automatic throttle valve.

Gas flow through the chamber can either be continuous, with sufficient velocity to ensure new gas for each RF pulse, or be pulsed synchronously with the RF, in which case the gas composition can be uniquely selected for each pulse. Further details can be found in [1, 2].

The electrode configuration used has a significant effect on the induced DC bias on the RF electrode. In particular, the standard parallel electrode arrangement results in typical bias values of 2-3 kV, whilst the hollow cup electrode (Figure A.1) can reduce this to ~ 200-300 V. In order to obtain high quality films, it was found necessary to place the substrate in the hollow cup RF electrode; higher bias values causing sputtering of the film. Several electrodes of different dimensions were used, but typical dimensions were: external diameter 108 mm, internal diameter 86 mm, depth 20 mm, with a conformal insulator of external diameter 129 mm. The electrode top plate was 5 mm thick with a centre hole 49 mm in diameter.

A2   PROCESS DEVELOPMENTS DURING THIS PROGRAMME

A2.1 Vapour Handling

With the great emphasis in this programme on vapour sources
with vapour pressures between 3 and 200 Torr at room temperature,
significant effort has been put into improving the handling of these
sources. A recently developed vapour flow controller from Vacuum General,
the LC2, has been installed on the plant on a 0.5 inch vapour line with its
own heated Baratron pressure gauge. Since it runs internally at 70°C,
vapours up to this temperature can be handled. However, the in-line
impedance of this controller is so low (2 orders of magnitude below normal
flow controllers) that all the vapours have been handled at room
temperature, greatly improving reliability and ease of operation. Gas flow
factors for the vapours have been derived by measuring the rate of pressure
rise in a known volume. The values derived are:

TMA (trimethylaluminium)	0.037 ± 15%
DEZ (diethylzinc)	0.17 ± 15%
TMG (trimethylgallium)	0.23 ± 15%
DMC (dimethylcadmium)	0.30 ± 15%

(NB. TMA is thought to be dimeric under the conditions of test and use).

Stable (calibrated) flow rates of above 100 sccm from room
temperature source bottles can easily be obtained with TMA, an order of
magnitude better than was previously possible.

A2.2 Reactor Chamber

When using high power and a hollow RF electrode to control the
bias, arcing at the walls of the 4-inch, 6-way cross reactor chamber
sometimes became a significant problem. This was considered to be due
largely to the relative sizes of the electrodes to the chamber, and so
rather than reduce the electrode size, which reduces the effectiveness of
the hollow electrode design, the reactor was replaced with a 6-inch, 6-way
cross. Arcing problems have been substantially reduced by this

modification.

A2.3 Safety Aspects

Phosphine has been used extensively during the preparation of LWIR super phosphides, and many safety precautions were taken at the onset of the work and others developed during it. The main features are given in Appendix C.

A3   REFERENCES

1)   G. Scarsbrook, I. P. Llewellyn, S. M. Ojha, R. A. Heinecke, Vacuum 38(8/10), 1989, p627.

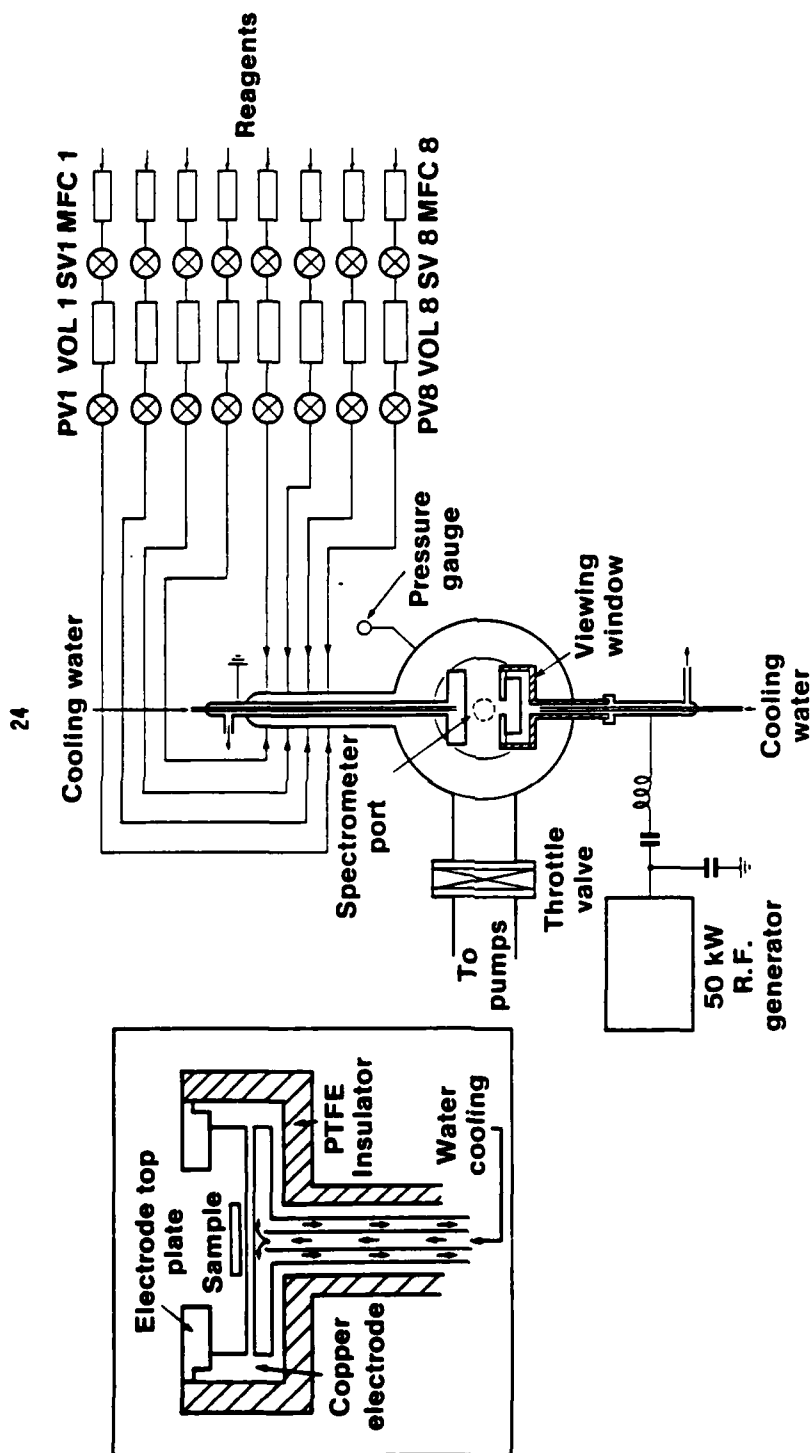2)   G. Scarsbrook, I. P. Llewellyn, R. A. Heinecke, J. Vac. Sci. Technol. A 7(3), June 1989, p1099.

Figure A.1: Pulsed Plasma Capacitive Reactor

APPENDIX B

PHOSPHORUS - THE ANION FOR LWIR MATERIALS

B1   INTRODUCTION

The pulsed plasma development of new IR materials began in 1987 under this ONR programme, looking at the model system GeP_xS_y. The early results indicated that this amorphous material exhibits a reasonably sharp optical cutoff, with a sufficiently high band gap to limit free electron absorption in the IR. In addition, its chemical stability was shown to vary with composition, increasing to a high level with phosphorus content up to GeP_x:x=3.5 or more. These results prompted a review of the field of amorphous polyphosphides, given in this appendix, and the selection of a range of potentially suitable cations for which volatile sources could be found. Both the theoretical and experimental studies have confirmed the uniqueness of phosphorus and the polyphosphides, and their potential in IR window applications.

Any study for new IR materials has to find a compromise between:

i) The need for weak covalent structures, with low co-ordination and heavy atoms, which push the phonon absorption bands out beyond the far infrared requirement.

ii) The need for strength, and a large band gap to limit free electron absorption at higher temperatures.

This appendix shows why amorphous phosphorus-rich phosphides have a major potential in fulfilling these requirements.

Phosphorus is the heaviest trivalent anion available which has no d electrons. Its weight moves the phonon bands further into the far infra-red, whilst its trivalent bonding allows three-dimensional network forming (unlike divalent sulphur). Absence of d electrons enhances the

mechanical properties and the band gap.

The choice of phosphorus is influenced by the amorphous nature of the films we deposit. Being trivalent, not only can phosphorus form amorphous three-dimensional networks, but these are not as strained as those of the tetravalent elements such as silicon, because of the reduced constraints. Elemental phosphorus forms a large number of allotropes, with widely varying properties. White phosphorus, for example, is formed from highly strained tetrahedral P_4 molecules weakly bonded together, resulting in a highly reactive material. In contrast, black phosphorus forms long range structures in both crystalline and amorphous forms, and is quite stable. Pulsed plasma deposited phosphides are more nearly related to black phosphorus, and can also show good stability.

B2   CONVENTIONAL PHOSPHIDES

The various crystalline phosphides differ greatly in their physical and chemical properties. These differences can, to a degree, be related to their structural geometry. The great majority of established phosphides range in composition from M_3P to MP_3, with most metals forming at least one compound in this range. They are classified as metal rich (P<60%) or phosphorus rich (P>60%) with the monophosphides in the middle. Metal-rich phosphides are usually hard, brittle, and electrically conductive, and have high thermal and chemical stability. Phosphorus-rich varieties are typified by lower melting points, much lower thermal stability, and are usually semiconductors. On heating, phosphorus-rich compounds revert to metal-rich compounds, with the evolution of phosphorus. The structures adopted by metal-rich compounds appear to be influenced mostly by radius ratio factors, whereas valency electrons and directive covalent bonds are more significant in the P-rich varieties. Some phosphides of groups I and II metals are decomposed by water to produce phosphine and are believed to have some ionic bonding.

B2.1 Monophosphides and Related Phosphides

The crystalline monophosphides BP, AlP, GaP and InP form a series of isomorphs with the zinc blende type structure. In these, each

atom is tetrahedrally co-ordinated by atoms of the other type to form a
continuous 3-D covalent structures. These monophosphides all have
semiconductor properties and their high carrier mobility and wide band gaps
suggest their use at high temperatures. They all have high thermal
conductivities.

Phosphide	Density (gcm^{-3})	Melting point (°C)	Hardness (Moh's)	Lattice Spacing (Å)	Thermal Cond. $(Wm^{-1}K^{-1})$
BP	2.89	2500	9.5	4.538	4000
AlP	2.42	1800	5.5	5.451	1300
GaP	4.10	1467	-	5.436	1000
InP	-	1058	-	5.87	-

B3   THERMAL CONDUCTIVITY IN PHOSPHORUS-RICH PHOSPHIDES

Amorphous materials are generally considered to be poor thermal
conductors, whereas high thermal conductivity is required for most IR dome
applications. However, it is probable that these unique phosphorus-rich
phosphides show higher thermal conductivities than other amorphous
materials.

The effect on thermal conductivity in going from a crystalline
material to amorphous material is to limit the mean free path of the
phonons to the scale of the chemical unit (probably of the order of a P_4
unit in white phosphorus, for example), thus reducing the thermal
conductivity K.

$$K = \frac{1}{3}C_v l v$$

where v = velocity of sound
      C_v = the specific heat
      l = phonon mean free path

Typically, for a crystalline material, l is limited by the
sample bounds up to about 10 K, resulting in a T^3 dependence of
conductivity on the specific heat. Above this temperature, the

conductivity rapidly falls due to phonon-phonon interactions, reducing the mean free path. In an amorphous material, the initial rise is of T^2 dependence, and continues to rise above 10 K, so that as T increases to 100 K and 1000 K, the two conductivities are converging. However, the thermal conductivity of amorphous materials near room temperature is typically 1 or 2 orders of magnitude down on its crystalline counterpart.

For the polymeric phosphorus structures, the distinction between crystalline and amorphous is much weaker, so that the loss of thermal conductivity on going to amorphous materials may be proportionately less. We can then anticipate a thermal conductivity on the lower end of the scale between that of the crystalline monophosphide (very much higher than ZnS), and that of the elemental amorphous black phosphorus (13.2 $Wm^{-1}K^{-1}$, slightly lower). Clearly the thermal conductivity is an important parameter to measure, but it is likely to be particularly sensitive to composition and preparation details (i.e. structure).

B4   THE STAUFFER PATENT

This summary of the Stauffer patent, brought to our attention by Dr. J. A. Savage, RSRE, is an illustration of some of the unique properties of the polyphosphides.

UK Patent: GB2 113 663A
Applicant: Stauffer Chemical Company, Westport, Connecticut, USA
Subject: High phosphorus polyphosphides
             i.e. MP_x where M = alkali metal (Li, Na, K, Rb, Cs)
                                or metals with similar bonding
             and x = 7 - 15
             or   x >> 15

(polyphosphide implying dominated by polymeric P-P bonding).

The materials are characterised by their useful properties:

-     Stability
-     Bandgap 1.4-2.2 eV, typically 1.8 eV

- High inherent resistance, but with ability to be doped (using Ni).
- Good photoconductivity
- Efficient luminescence
- Ability to form a rectifying junction

These single-crystal properties are also retained in the amorphous state.

The crystalline form of the polyphosphides of type MP_{15} consists of a phosphorus skeleton of parallel tubes of pentagonal cross-section, linked by P-M-P bridges. The useful electrical and optical properties of MP_{15} materials are preserved in the MP_x (x>>15) materials, being dominated by the P-P bonding of the phosphorus skeleton which has an average co-ordination number a little less than 3. Since K does not form lower phosphides than KP_{15}, unlike the other alkalis in the KP_x system, is easier to control, and is therefore the preferred system The formation of amorphous KP_{15} is also found to occur under any deposition conditions where the temperature is not sufficiently high to cause crystallisation, and high enough that KP_x, x >> 15, is not deposited. In both the crystalline and amorphous MP_{15}, the local order is the same, that of locally parallel elongated phosphorus tubes with pentagonal cross-section, double layers of the tubes being held together by interstitial alkali metal atoms. P-P bonds are 12.13 to 2.58 Å, with a bond angle of 87° to 113°, average 102°.

The Role of the Metal

The many allotropes of phosphorus illustrate its structural versatility, and the metal atoms are believed to contribute by making more stable the particular structure which is desirable. Clearly only a small amount of metal is required. Apart from the alkali metals, tubular phosphorus structures have been reported in 2b-4a-P_{14} compounds (2b=Zn, Cd, Hg, and 4a=Sn, Pb).

Mechanical Properties

MP_x materials, particularly MP_{15}, can be deposited as amorphous films with good adhesion to metals and glass. The films are ductile, non-porous, polymeric and non-brittle.

B5   SUMMARY

It is concluded that:

1)   Phosphorus can form very stable, hard materials in binary and higher compounds.

2)   Phosphorus is heavier than nitrogen and oxygen, and forms weaker bonds, so that many M-P (M = metal or cation) bonds do not show phonon absorption at less than 12 μm.

3)   Conversely, phosphorus has no d electrons, and forms harder, more stable compounds with wider bandgaps than the other pnictides.

4)   The critical thermal properties, particularly the conductivity, can potentially exceed those of ZnS, but will be sensitive to the exact material composition. Consequently this parameter should be refined after other less sensitive parameters have been used to select the particular materials of interest.

B6   BIBLIOGRAPHY

1)   Structural Chemistry of Phosphorus, D.E.C. Corbridge, Elsevier, Scientific Publishing Company, London, 1974.

2)   The Structure of the Elements, Jerry Donohue, Wiley-Interscience, London, 1974.

3)   UK Patent: GB2 113 663 A, Stauffer Chemical Company, Westport, Connecticut, USA. On High Phosphorus Polyphosphides.

4)   Encyclopedia of Chemical Technology, 3rd Ed., Volume 17, Editorial Board H.F. Mark, D. F. Othner, C. G. Overberger, G. T. Seaberg, Pub. Wiley-Interscience, 1982.

APPENDIX C

PHOSPHINE SAFETY-MEASURES IN PACVD PROCESSING

C1   INTRODUCTION

STL's unique pulsed plasma deposition process has been used in the development of new LWIR materials, because of its ability to rapidly create new materials from gaseous precursors. Many of these precursors are toxic, particularly the hydrides and the organometallics. Whilst phosphine is not the most toxic of the hydrides used, it presented the greatest hazard since it has been used in the greatest quantity (2-3 kg per year, over - 3 years).

The toxicity limit value (TLV) of phosphine is 0.3 ppm, but its initial odour threshold is much lower (by $> 10^1$) than this, making it unlikely that personnel could be exposed to a toxic level suddenly without detecting it. Extended exposure does dull the sensitivity (olfactory fatigue), so it is important to monitor working and storage areas.

The extent of the hazard to prolonged low exposure to phosphine is uncertain, though recent research suggests genetic damage may occur with exposure levels below but near TLV [1]. The short term symptoms of exposure are reasonably well documented (faintness, apathy, nausea, vomiting etc.), and severe exposures resulting in permanent injury and death have been reported [2].

The initial policy of this programme was to build in all safety precautions which were evident at the time. Experience, together with the recent publications, prompted further measures to be installed.

C2   INITIAL PRECAUTIONS

C2.1 Gas Monitoring

Hydride monitoring equipment was installed on each plasma

machine, also in the two gas storage huts. This equipment is of the paper
tape variety (MDA TLD-1), allowing easy testing and servicing together with
a guaranteed maximum reliability. With several hydrides present in the
laboratory, these instruments were calibrated for the TLV level of germane,
which is the most difficult to detect, resulting in a much lower than TLV
threshold for the other hydrides including phosphine.

In addition, a small portable hand sniffer (Union Carbide Gas
Leak Detector) was purchased. Its main application is for 'sniffing' for
hydrogen as a method of isolating minor leaks, but it is also capable of
detecting phosphine.

C2.2 Source Gas Handling

Specialist gas storage huts, in the open with full extraction
and monitoring, were constructed by STL site services to hold the source
cylinders. Gas lines into the plasma processing cleanroom were constructed
from fully welded stainless steel tubing, with bellow sealed valves.
Specialist gas pressure regulators were installed, with cross purging using
argon and pumping down to vacuum. All lines were fully pressure tested and
vacuum tested, and vacuum testing is incorporated into the cylinder change
procedure.

C2.3 Waste Gas Handling

Exhaust gases from the process are passed through a toxic gas
scrubber, before emission well above roof level. Initially, this scrubber
was the simple charcoal barrel absorption type which was effective but of
insufficient capacity for long term utilisation. This was replaced by a
wet scrubber (Mystair) which is fully self-dosing and monitoring, and
capable of removing phosphine to below the sensitivity of the MDA gas
detector (< 10 ppb) before > 1000:1 dilution in air and fan driven emission
well above roof level.

C2.4 Plasma Deposition Machine

Partly as a requirement for containing the RF, the plasma

reactor was entirely enclosed within a metal closure, and this cabinet was then air extracted. In addition, the pumping stack was also enclosed and air extracted, partly because of the risk of a vacuum pump explosion when using silane. Maintenance of the rotary pump (e.g. oil change) was performed using a small self-contained breathing set.

The main hazard associated with the reactor chamber was considered to be dust particles (since it is regularly taken down to vacuum), and nose/mouth dust masks were worn as appropriate. All parts were removed to a nearby fume cupboard for cleaning and storage. Since some phosphides are unstable in moist air, back extraction through the chamber was fitted to operate when the chamber was up to air.

C2.5 Procedures and-Staffing

The safe operation of the equipment relies above all on safe procedures and competent staff. Only fully qualified personnel versed in all the necessary routine and emergency procedures are allowed access to the plasma machines. Working procedures includes the use of gloves for any handling of samples and maintenance work.

C3 ADDITIONAL PROCEDURES

Experience in handling phosphine prompted these additional procedures:

C3.1 Additional Extraction of Chamber Enclosure

An improved extraction facility, to the standard of a conventional fume cupboard, was fitted to the reactor enclosure. This was designed to greatly reduce both gaseous and particle emission from the chamber area.

C3.2 Regular Cleaning of Chamber Enclosure

In addition to improved extraction, the reactor enclosure was made as empty as possible to allow effective regular cleaning. A

specialist toxic waste vacuum cleaner was installed, with a HEPA filter and extraction on its exhaust, to vacuum clean the chamber enclosure. Following this the chamber area is wiped over with damp paper cloths which are then disposed of as hazardous waste.

C3.3 Full Working Breathing Apparatus

Whilst not a safety feature for normal working, a two man, trolley based, self-contained breathing set is being purchased (this has been delayed by the revision of the British Standard covering this equipment). The principal application of this equipment will be on servicing major items (e.g. pumps, vacuum components).

C3.4 Lightweight Filtered Air Hood

During minor chamber modifications and electrode changes, it is difficult for the operator to work without his head within the chamber enclosure. For this purpose, a powered, filtered air respirator with lightweight hood is used. The power pack and filter are mounted on the user's back, keeping the air intake away from the potentially contaminated area.

C3.5 Automatic Oil Change

The rotary pump used for this work is an Edwards E2M40 mineral oil pump. Whilst fomblinised pumps are often recommended for handling silane and other hydrides, the improved reliability of mineral oil pumps over fomblinised pumps is of prime importance because of the contamination problem. However, the mineral oil pumps need a regular oil change, which exposes the oil to the cleanroom atmosphere. Consequently, an automatic oil change system has been devised and fitted, which allows removal of the contaminated oil into a sealed container and introduction of new oil without any exposure to the cleanroom atmosphere. Its principle of operation is to entirely isolate the pump and pressurise the casing with nitrogen to force the old oil into a container, and then to extract the pump and pressurise a new oil feeder tank to refill the pump. Fig. C.1 shows a schematic of this system. Isolating the pump involves closing the

exhaust port, so this valve is carefully interlocked so that it cannot close whilst the pump is running, since the pump could otherwise easily blow itself apart.

C3.6 Exhaust Line Oil Mist Filters

The original specification for the gas scrubber included inlet oil mist filters to trap any oil mist from the rotary pumps. The scrubber manufacturer stated that these were not necessary, and they were not originally fitted. However, experience has shown that oil mist can ultimately be transferred to the outlet of the scrubber, still containing 'unscrubbed' phosphides/phosphine. Fitting proper inlet oil mist filters has removed this problem. It is recommended that oil mist filters are always specified in the purchase of a wet gas scrubber.

C3.7 Full Washing Facilities Locally

Since phosphine can be detected at very low limits, it was found that, despite using gloves, particles of phosphides could get onto the hands and start decomposing, causing them to smell. Whilst limited washing facilities were already in the laboratory, in addition to nearby toilet facilities, these were substantially upgraded to enable and encourage regular washing.

C3.8 Disposal Cleanroom Garments

Work which involved significant disassembly of the equipment (e.g. electrode change or chamber cleaning) was found to carry risk of transferring phosphide particles to the operators' cleanroom garments, and even ultimately to their clothes. The latter was particularly of concern, being a significant health hazard and also a potential embarrassment; sweating would cause the unstable phosphide particles to decompose and emit phosphine, giving the operator a distinct odour. In addition to placing extra emphasis on maintaining the cleanliness of the reactor cabinet during such work, and on improving working procedures, it was found advantageous to use a new disposable cleanroom garment (Tyvek coveralls) for each entry into the cleanroom.

C3.9 Blood Testing

Following receipt of reference [1], staff associated with the programme of developing the super-phosphides were tested for genetic damage, as a precautionary measure additional to the safety measures detailed above. Some difficulty was experienced in finding a laboratory capable of performing the required tests, but they were finally carried out at the Queen Elizabeth Hospital for Children (Hackney Road, London, E2 8PS).

Cultures from the blood samples were established in media designed to reveal chromosome breaks and rearrangements as evidence of chromosome damage. The analysis was performed by G-banding the resulting slides, and by special treatment using DNA antigonists to show the degree of breakage and exchange between sister chromosomes compared with controls.

The results showed no genetic abnormality for any of the workers tested.

This blood testing is not being used routinely in this programme since the approach adopted is to reduce exposure levels to an absolute minimum. Exposure above previous levels would be readily detectable, and the main risk of genetic damage is now considered to be from a major incident rather than continued low exposure.

C4   CONCLUSIONS

Phosphine is a highly toxic gas which needs to be handled with extreme caution. Its strong odour is a useful safety indicator, but cannot be relied on in an enclosed environment because of olfactory fatigue. By implementing strict safety measure, and enforcing high levels of staff discipline, phosphine can be used with acceptable levels of safety.

Whilst considerable thought went into safety during the initial setting up of the LWIR materials programme, experience of handling phosphine has evolved several further techniques for its safe handling.

C5 REFERENCES

1) V. F. Garry, J. Griffith, T. J. Danzl, R. L. Nelson, E. B. Whorton, L. A. Krueger, J. Cervenka, Science, 13th October 1989, p187.

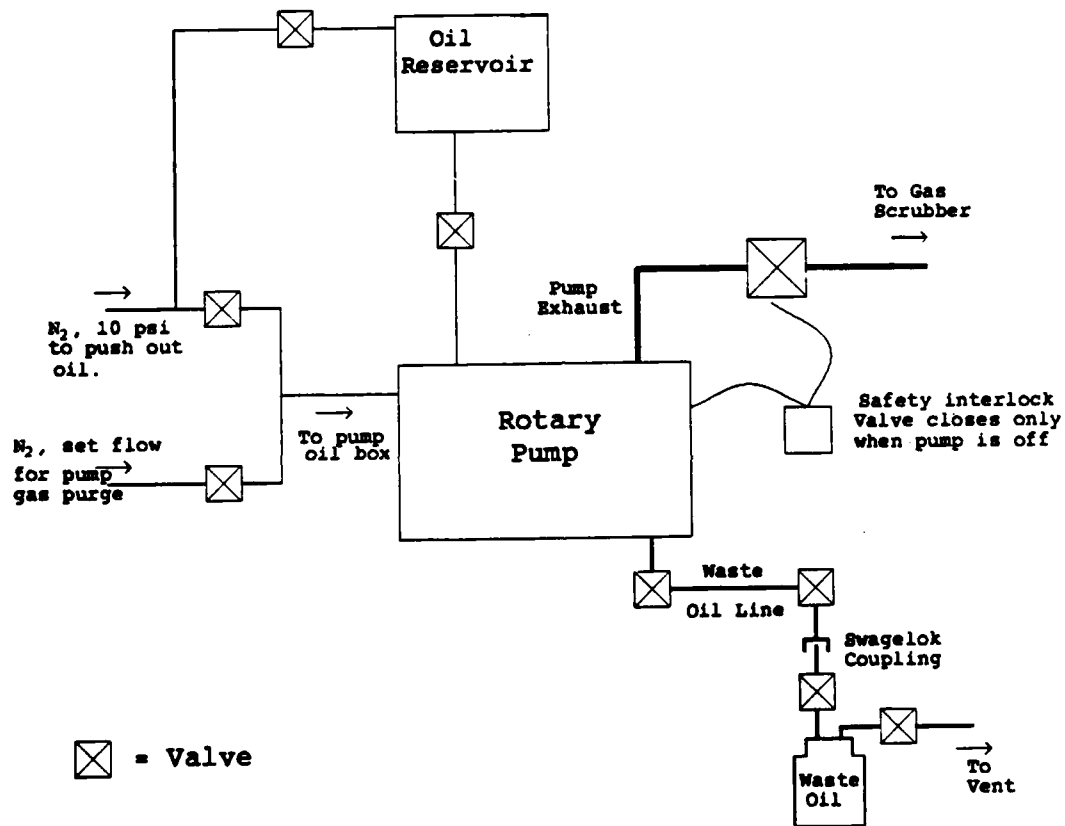2) R. Wilson, F. H. Lovejoy, R. J. Jaeger, P. L. Landrigan, JAMA (Journal of the American Medical Association) 244(2), 1980, p148.

Figure C.1: Automatic Oil Change System